(12) UK Patent Application (19) GB (11) 2 174 697 A

(43) Application published 12 Nov 1986

(21) Application No 8608680

(22) Date of filing 10 Apr 1986

(30) Priority data
(31) 3515403 (32) 29 Apr 1985 (33) DE

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(51) INT CL[4]
C07C 69/24 67/02

(52) Domestic classification (Edition H):
C2C 20Y 236 240 263 30Y 366 368 37X 491 628 AC CB

(56) Documents cited
None

(58) Field of search
C2C

(54) A process for the catalytic transesterification of fatty acid glycerides with lower alkanols

(57) Solid sodium carbonate and/or sodium hydrogen carbonate is/are used as heterogeneous solid catalyst(s) in the transesterification of de-acidified and anhydrous fatty acid glycerides, more especially from fats and/or oils of natural origin, with lower monofunctional alcohols to form fatty acid alkylesters and glycerol.

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SPECIFICATION

A process for the catalytic transesterification of fatty acid glycerides with lower alkanols

This invention relates to an improved process for the production of esters of fatty acids or fatty acid mixtures and lower monofunctional alcohols by catalytic transesterification of fatty acid glycerides with the lower monofunctional alcohols in the presence of basic catalysts. Suitable lower, monofunctional alcohols are, in particular, the corresponding C_1-C_4 alcohols, particular significance being attributed in practice to methanol. Fatty acid glycerides in the context of the present invention are corresponding triglycerides or partial esters of fatty acids or fatty acid mixtures and glycerol. Of particular importance in this respect are the triglycerides and, above all, fats and/or oils of native origin which may be readily converted into fatty acid methylesters by the process according to the invention.

Fatty acid methylesters are of considerable commercial significance as starting material for the production of fatty alcohols and other oleochemical products, such as ester sulfates, fatty acid alkanolamides and soaps. On an industrial scale, the fatty acid methylesters are mainly produced by catalytic transesterification (alcoholysis) of fatty acid triglyceride mixtures of the type present in fats and oils of vegetable and/or animal origin.

Various tried and tested processes are available in practice for this transesterification. The choice of the particular process conditions is governed to a large extent by the quantity of fatty acids present in the triglycerides.

Native fats and oils almost always contain considerable quantities of free fatty acids, the corresponding value being variable within wide limits in each individual case, depending on the origin of the material and its previous history, and almost always being above 3% by weight.

It is known that fats and oils having a relatively high content of free fatty acids may be transesterified in the presence of alkali or zinc catalysts to form the corresponding fatty acid methylesters, the reaction being carried out at 240°C under a pressure of approximately 100 bar using a 7- to 8-fold molar excess of methanol (Ullmann, Enzyklopadie der technischen Chemie, 4th Edition, Vol. 11, 1976, page 432).

It is also known that fats and oils can be reacted with a limited excess of monofunctional alcohols at the lower temperatures of 25 to 100°C, under normal pressure and in the presence of alkaline catalysts to form the corresponding fatty acid alkylesters and free glycerol. A corresponding process is described as the first step of a soap manufacturing process in US-PS 2 360 844. The basic catalysts used in this process are alcoholic solutions, more especially methanolic solutions, of NaOH or KOH (caustic soda or potash) or corresponding alcoholic solutions of sodium or potassium methylate. In this case, therefore, the basic catalyst is homogeneously dissolved in the reaction mixture and is consumed in the further course of the process for forming the corresponding sodium or potassium fatty acid soaps.

However, this alkali-catalyzed pressureless transesterification of fatty acid glycerides to the corresponding fatty acid alkylesters requires the use of fats or oils which are virtually or substantially anhydrous and of which the free fatty acid content is less than 0·5% by weight (corresponding to an acid number of about 1). Since relatively large quantities of water and fatty acids are almost always present in industrial fats and oils, the pressureless transesterification presupposes drying and, almost always, a pretreatment to reduce the acid number, in which the acid number of the starting material is reduced to the necessary extent, for example by conversion of the free fatty acids present into the corresponding alkyl or glycerol esters.

This pre-esterification of acid-containing fatty acid glycerides may be carried out in various ways. For example, it may be carried out in the presence of alkaline catalysts at temperatures beyond 240°C and under a pressure of 20 bar (Ullmann, Enzyklopadie der technischen Chemie, 4th Edition, Vol. 11, 1976, page 432). However, this method of pre-esterification with methanol again presupposes the use of expensive reactors. It is also known that esterification of the free fatty acids in the oil may be carried out with added monofunctional lower alcohols, especially methanol, in homogeneous phase using acid catalysts, for example p-toluene sulfonic acid. In this case, however, the catalyst has to be subsequently separated off and the water removed by washing the pre-esterified oil with methanol. The problems arising here are dealt with, for example in DE-OS 33 19 590 (D 6757 US). An improved process for reducing the content of free acids in fats and/or oils by treating them with a lower monoalcohol in the presence of acids as transesterification catalysts is describ d in Applicants' arlier U.K. Patent Application 86 00478 ("a process for the pre-esterification of free fatty acids in crude fats and/or oils"). This process is characterized in that solid cation exchanger resins in acidic form are used as catalysts. In this process, therefore, the catalyst is pr sent as a het rogen ous solid phase which may be separated off without difficulty from the reaction mixture.

The teaching behind the present invention is based on the premise outlined at the beginning that fatty acid glycerid s may readily be reacted with lower monofunctional alcohols, particularly methanol, in the presence of basic catalysts and under mild reaction conditi ns, particularly at

ambient pressure, l w t mp ratures and with a low methan l input to form the corresponding alkylesters and free glyc rol and that, in addition, sufficient practical possibilities are available for meeting the necessary requir m nts, namely low free fatty acid and water contents of the starting material. The inventors set themselves the task of modifying this bas -catalyzed transesterification of the fatty acid glycerides with monofunctional alcohols, particularly methanol, in such a way that the reaction may be catalyzed by solids which are substantially insoluble in the starting material or rather in the reaction mixture, i.e. may be heterogeneously catalyzed. It is clear that the transesterification process is considerably simplified in this way, particularly in regard to separation of the catalyst from the reaction mixture.

The solution provided by the invention is based on the surprising observation that solid sodium carbonate Na_2CO_3 and/or sodium hydrogen carbonate $NaHCO_3$ as heterogeneous solid catalysts are capable of effectively catalyzing the desired, alcoholytic splitting of fatty acid glycerides under the mild conditions known per se, particularly low temperatures and pressures.

In a first embodiment, therefore, the present invention relates to the use of solid sodium carbonate and/or sodium hydrogen carbonate as heterogeneous solid catalysts in the transesterification of de-acidified and anhydrous fatty acid glycerides with lower monofunctional alcohols to form fatty acid alkylesters and glycerol.

In another embodiment, the invention relates to a process for the catalytic transesterification of fatty acid glycerides with lower monofunctional alcohols by reaction of a substantially acid-free and water-free glyceride starting material with the monofunctional alcohol, preferably followed by separation of the glycerol released. The new process is characterized in that solid sodium carbonate and/or solid sodium hydrogen carbonate is/are used as heterogeneous solid catalyst(s). In the preferred embodiment, the process according to the invention is carried out under cost- and energy-saving conditions in that the reaction of the fatty acid glyceride starting material is carried out at or around normal pressure and at only moderately elevated temperatures which, in particular, do not significantly exceed the 100°C mark. In addition, the preferred measures of keeping the excess of the monofunctional alcohol low, separating the reaction mixture by physical phase separation and preferably using distillation-based separation steps only where they are unavoidable all contribute in particular towards achieving the object of reducing costs.

The temperature at which the transesterification process is carried out is preferably around the boiling temperature of the alkanol used. Since the transesterification is carried out at normal pressure or at only slightly elevated pressures, the reaction temperature prevailing during transesterification of the glycerides with methanol is normally in the range of from about 60 to 75°C and preferably in the range of from about 65 to 70°C.

Suitable fatty acid glycerides are, in particular, correspondingly pretreated (de-acidified) fats and/or oils of vegetable and/or animal origin. They are subjected to transesterification with lower alkanols preferably containing from 1 to 4 C-atoms. Methanol is preferably used as the lower alkanol. The glyceride starting material should have an acid number of at most about 1, preferably of at most about 0.7 and more preferably of the order of 0.5 or lower. The water content of the glyceride starting material should be as low as possible, in particular, should amount to no more than about 0.8% by weight, substantially anhydrous conditions being preferred. De-acidified and anhydrous glyceride starting material may readily be obtained as the reaction product of the above-described preliminary process steps, more especially as the product of pre-esterification of the starting material.

According to the invention, the excess of monofunctional alcohol which is used in the transesterification of the glycerides is also kept as small as possible. In the preferred embodiment, ratios by weight of alkanol, preferably methanol, to the fatty acid glyceride of from 0.2 to 1:1 and, more preferably, of from 0.2 to 0.5:1 are used in the reaction mixture.

Any known process modifications may be employed for the practical application of the sodium carbonate and/or sodium hydrogen carbonate present in heterogeneous solid phase. The heterogeneously catalyzed transesterification reaction may be carried out either in batches or even continuously. The catalyst may be used either as a relatively fine or relatively coarse powder, in the form of chips or tablets or even as an impregnating catalyst applied to a support. The catalyst material may be arranged in the form of a fixed bed, although it is also possible to use the catalyst material in the form of a moving mass, for example in stirrer—equipped vessels, in moving beds or fluidized beds in pulsators and the like. It is particularly appropriate to carry out the heterogeneously catalyzed transesterification under normal pressure with gentle boiling of the alcohol.

The glycerol releas d is removed from the reaction mixture, preferably by phase separation. To this end, it may be advisabl to co l the reaction mixture or a sidestream branched off from the reaction mixture. In this connection, it is of advantag to evaporate some of the monofunctional alcohol from the reacti n mixtur or from the sid stream of the reacti n mixture before cooling. This reduces the solubility of the glycerol released in the fatty acid/alcohol/oil phase and, at the same time, increases the density of the glycer l phase, so that the glycerol f rmed may readily

be removed by phase s paration. The alkanol removed from the reacti n mixture in this way is preferably recirculated to the reactor. Where this procedur is adopted, the partial removal of the glycerol from the reaction mixture is achiev d in that, where a sidestream is branched ff, more especially continuously, from the reactor, the methylester/oil phase r turned to the reactor is a homogeneous liquid phase by virtue of the removal of methanol and the subsequent separation of free glycerol from the sidestream, i.e. neither a separate methanol phase nor a phase consisting of free glycerol occurs in the recycled liquid phase.

Accordingly, a particularly preferred embodiment of the invention is characterized in that, where the process is carried out continuously, at least one sidestream of the reaction mixture is first passed through an evaporator in which any free alkanol present is at least partly evaporated. The liquid phase is then cooled to temperatures below 50°C and more especially to temperatures in the range from 30 to 40°C, after which the heavier glycerol phase is separated off by phase separation and removed from the circuit, whilst part of the lighter ester phase is returned as a recycle stream to the transesterification stage into which the evaporated alkanol and fresh reactants are simultaneously introduced. The separation of the glycerol phase from the recycle stream may be facilitated by additional separation aids, for example by using coalescence separators. Together with the glycerol phase, any water and soaps present or accumulating are removed from the reactor.

In one preferred embodiment of the process according to the invention, the transesterification is carried out in several stages in a cascade of reactors.

The process according to the invention is particularly suitable as an important process step in the working-up of natural, more especially impure, fats and/or oils, such as coconut oil, palm kernel oil, soya oil, tallow and the like. There is no need for these starting materials to be purified to remove the sludges and slimes naturally present in them. The natural starting material is first preesterified, as described at the beginning. The process according to Applicants' earlier U.K. Patent Application 86 00478 (D 6972; "a process for the pre-esterification of free fatty acids in crude fats and/or oils"), which is carried out with solid cation exchanger resins, is particularly suitable for this purpose. In addition to the excess methanol from the pre-esterification, the material obtained in this preliminary stage, which preferably has acid numbers below 0.7, also contains fractions of water which may be completely or partly removed in the form of a mixture. This removal of the water of reaction from the pre-esterification step provides the process according to the invention with a starting material which may be directly transesterified in accordance with the invention. The sludges and slimes present do not have to be separated off beforehand. They are automatically removed during the necessary working-up by distillation of the fatty acid methylesters formed in accordance with the invention.

EXAMPLES

EXAMPLE 1

In a stirrer-equipped reactor (stirrer speed n=350 r.p.m.), 1000 g of pre-esterified coconut oil (acid number of the treated material 0.57) and 500 g of methanol were reacted over a period of 1 hour in the presence of 10 g of Na_2CO_3 powder, the reaction being carried out under normal pressure with gentle refluxing of the condensate (reaction temperature 69°C). After cooling and settling of the glycerol phase, the quantitative ratio of the fatty acid methylester phase to the glycerol phase was 3.1:1. The content of bound glycerol in the fatty acid methylester phase had fallen from 13% by weight to 0.2% by weight.

EXAMPLE 2

In a 2.5 liter capacity, stirrer-equipped reactor (stirrer speed 800 r.p.m.), 2 kg of pre-esterified anhydrous coconut oil and 1 kg of methanol were reacted intermittently for 2 hours with gentle boiling. 400 g of dried soda chips (average particle size 1 to 5 mm) were whirled around in the reaction mixture as catalyst. 0.5 l/h of pre-esterified coconut oil (acid number 0.43; 13% by weight bound glycerol) and 0.24 l/h of methanol were then continuously delivered to the reactor. A recycle stream of 5.6 l/h was run off from the reactor and largely freed from the methanol in an evaporator. After cooling to 35°C, a relatively heavy glycerol/methylester phase was removed from this recycle stream in a separator through a control valve so as to maintain a constant liquid level in the reactor. The remaining phase, a fatty acid methylester phase of low glycerol content, was returned to the reactor in the form of a recycle stream. The methanol separat d off in the evaporator was also recycled to the reactor. The reaction in th react r took place at normal pressure with gentle boiling f the methanol.

The relatively h avy glycerol/m thylester phase removed from the recycle stream in the first separator separated in a separation vessel int a glycer l phase and a fatty acid methylester phase. Under stationary conditions, the bound glycerol content of the methylester phase after separati n of the glycerol amounted t around 0.5% by w ight. The values were reproducible over several days without changing the catalyst.

CLAIMS

1. A process for the transesterification of de-acidified and anhydrous fatty acid glycerides, with lower monofunctional alcohols to form fatty acid alkylesters and glycerol in which s dium carbonate and/or sodium hydrogen carbonate ar used as heterogene us solid catalysts.

2. A process as claimed in Claim 1 in which the fatty acid glycerides are obtained from fats and/or oils of natural origin.

3. A process as claimed in Claim 1 or Claim 2 in which the de-acidified glyceride starting material is reacted with the alkanol at or around normal pressure and at moderately elevated temperatures.

4. A process as claimed in Claim 3 in which the moderately elevated temperature corresponds approximately to the boiling temperature of the alkanol.

5. A process as claimed in Claim 3 or Claim 4 in which the solid catalysts are used in the form of a powder, or in the form of a particulate material applied to a support.

6. A process as claimed in Claim 5 in which the solid catalyst is used as a powder dispersed in a mixture of the reactants.

7. A process as claimed in Claim 5 in which the solid catalyst is used in the form of a fixed bed catalyst.

8. A process as claimed in any of Claims 1 to 7 in which the de-acidified, substantially anhydrous fatty acid glycerides have acid numbers of at most 1.

9. A process as claimed in Claim 8 in which the fatty acid glycerides have acid numbers of at most 0.7.

10. A process as claimed in any of Claims 1 to 9 in which the ratio by weight of alkanol to fatty acid glyceride in the reaction of mixture is in the range from 0.2:1 to 1:1.

11. A process as claimed in Claim 10 in which the ratio by weight of alkanol to fatty acid glyceride is from 0.2:1 to 0.5:1.

12. A process as claimed in Claim 10 or Claim 11 in which methanol is used as the alkanol.

13. A process as claimed in any of Claims 1 to 12 in which glycerol released in the reaction is removed from the reaction mixture by cooling and phase separation, alkanol initially being evaporated and a phase containing free glycerol then being separated off.

14. A process as claimed in any of Claim 1 to 13 which is carried out continuously and at least one sidestream of the reaction mixture is passed through an evaporator in which any free alkanol present is at least partly evaporated, after which the liquid phase is cooled to temperatures below 50°C the heavier glycerol phase is then separated off by phase separation and removed from the circuit whilst part of the lighter ester phase is returned as a recycle stream to the transesterification stage into which the evaporated alkanol and fresh reactants are simultaneously introduced.

15. A process as claimed in Claim 14 in which the liquid phase is cooled to a temperature of 30–40°C.

16. A process as claimed in any of Claims 1 to 15 in which the transesterification is carried out in several stages in a cascade of reactors.

17. A process as claimed in Claim 1 substantially as herein described with reference to the Examples.

18. The use of sodium carbonate and/or sodium hydrogen carbonate as heterogeneous solid catalysts in the transesterification of de-acidified and anhydrous fatty acid glycerides with lower monofunctional alcohols.

Printed in the United Kingdom for Her Majesty's Stationery Office, Dd 8818935, 1986, 4235.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.